

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : B32B 9/00	A1	(11) International Publication Number: WO 95/05939 (43) International Publication Date: 2 March 1995 (02.03.95)
(21) International Application Number: PCT/US94/08860 (22) International Filing Date: 4 August 1994 (04.08.94) (30) Priority Data: 08/111,800 25 August 1993 (25.08.93) US (71) Applicant: FMC CORPORATION [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US). (72) Inventors: SEWALL, Christopher, J.; Little Valley Farm, Apartment #5, RD#1, Canal Road, Princeton, NJ 08540 (US). RENN, Donald, W.; Brewster Point, Glen Cove, ME 04846 (US). RILEY, Peter, J.; Sherman's Point Road, Camden, ME 04843 (US). THOMAS, William, R.; 7 Gaylord Court, Newtown, PA 18940 (US). DUMONT, Lisa, E.; 8 Elm Street, Rockport, ME 04856 (US). CROSBY, Guy, A.; 74 Gallup Road, Princeton, NJ 08540 (US). (74) Agents: FELLOWS, Charles, C. et al.; FMC Corporation, 1735 Market Street, Philadelphia, PA 19103 (US).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: NONAGGREGATING HYDROCOLLOID MICROPARTICULATES, INTERMEDIATES THEREFOR, AND PROCESSES FOR THEIR PREPARATION (57) Abstract Substantially dry, rehydratable, water-dispersible, gel-forming, porous hydrocolloid microparticulates containing internally or externally and externally at least one water-soluble, non-gelling, hydration enhancing hydrocolloid, processes and intermediates for their preparation, and their uses.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

NONAGGREGATING HYDROCOLLOID MICROPARTICULATES,
INTERMEDIATES THEREFOR, AND PROCESSES FOR THEIR
PREPARATION

5 The present invention relates to microparticulate hydrocolloids, having particular utility as fat replacement components in comestibles.

10 The literature and patent records are replete with discoveries in the field of hydrocolloids, including microparticulate forms thereof.

 Many techniques have been used to prepare hydrocolloid microparticles, such as spray processes and emulsion processes. See, e.g. PCT WO 91/19424; EP-A
15 0437360 A1; U.S. 5,082,684; U.S. 4,956,128; J.C. Ogbanna et al., "Production of Micro-Gel Beads by a Rotating Disk Atomizer", J. Ferment. Bioeng. 68(1), 40-48, 1989; R.M. Buitelaar, A.C. Hulst, and J. Tramper, "Immobilization of biocatalysts in thermogels using the resonance
20 nozzle for rapid drop formation and an organic solvent for gelling", Biotechnology Techniques 2(2), 109-114, 1988; H. Su, R. Bajpai, and G.W. Preckshot, "Characterization of Alginate Beads Formed by a Two Fluid Annular Atomizer", Applied Biochemistry and Biotechnology,
25 20/21, 561-569, 1989; P. Audet and C. Lacroix, "Two-phase Dispersion Process for the Production of BioPolymer Gel Beads: Effect of Various Parameters on Bead Size and Their Distribution", Process Biochemistry, December 1989, 217-226; M.R. Chaudhari et al.,
30 "Preparation of Crosslinked Starch Beads as a Medium for Gel Filtration", Starch/Stärke, 41(11) 415-416, 1989; S. Hjertén, "The preparation of agarose spheres for chromatography of molecules and particles", Biochem. Biophys. Acta., 79, 393-398, 1964; Y. Motozato, "Beads of cross-
35 linked glucomannan and production thereof", U.S.

- 2 -

4,882,426 (11/21/89); and British Patent No. 1,577,955 to Takeda Chemical Industries.

In addition, the following references describe methods for encapsulating other materials within the microparticles:

U.S. 4,956,128 to Hommel et al.; U.S. 4,143,201; U.S. 3,936,573 to Brocket; I. Chibata, J. Kato, and M. Wada, "Method for Producing Ethanol with Immobilized Microorganism", U.S. 4,350,765 (9/21/82); M. Wada, J. Kato and I. Chibata, "A New Immobilization of Microbial Cells", Eur. J. Appl. Microbiol Biotechnology, 8, 241-247 (1979); A.R. Navarro, M.C. Rubio, and D.A.S. Callieri, "Production of Ethanol by Yeasts Immobilized in Pectin", Eur. J. Appl. Microbiol Biotechnology, 17, 148-151 (1983); K. Nilsson et al., "Entrapment of animal cells for production of monoclonal antibodies and other biomolecules", Nature, 302, 629-30, 1983; and K. Mosbach, and K. Nilsson, "A method of encapsulating bio material in bead polymers", PCT Application WO 83/03102 (9/15/83). U.S. 3,573,058 to Tiemstra discloses a co-dried mixture of microcrystalline cellulose and small quantities of a hydrocolloid. U.S. 4,192,900 discloses starch particles comprising starch mixed with a gelling hydrocolloid.

The following references relate to specialized techniques for drying hydrocolloid microparticulates in order to try to prevent agglomeration of the microparticulates which will otherwise occur:

British patent No. 887,901 to F. Hoffman-La Roche & Co. (CA 56, 9179 i(1961)) discloses emulsions of a gelling colloid, including pectin and algin, which are dried into particles by spraying or atomizing into a gas at least 10° below the t_m of the resultant gel, and the particles are kept separate in free fall for at least 15 seconds for gelling to begin. U.S. 2,438,450 to Nelson discloses a drying technique for microparticulates com-

- 3 -

prising mixing with the hydrated microparticulates a quantity of previously dried microparticulates to prevent agglomeration of the hydrated microparticles. V. Ghetie and H.D. Schell, "Drying of Agarose Gel Beads",
5 Experientia 27(12), 1384-5, 1971 discloses agarose microparticles which are acetone washed, then air dried at room temperature.

In addition to the above specialized drying techniques for minimizing agglomeration problems, other
10 techniques have been used to try to prevent agglomeration of hydrocolloid microparticles. For example, U.S. 5,153,020 to Singer et al., discloses water-dispersible spheroidal macrocolloid microparticles as a fat substitute with which "aggregate blocking agents" such
15 as lecithin, pectin, xanthan gum, and carboxymethylcellulose, are added to the macrocolloid particles to stabilize the particles in the hydrated form in which the particles are manufactured and employed as fat substitutes.

20 U.S. 4,911,946 discloses the use of aggregate blocking agents such as lecithin and xanthan gum in hydrated spheroidal carbohydrate microparticles to produce the mouth feel of fat/cream.

The following references disclose microparticles
25 containing an inner core which can be a hydrocolloid, and an outer hydrophobic coating of a digestible fat: U.S. 4,305,964; EP-A 0 011 345; and EP-A0 380 225.

U.S. 3,527,712 discloses a process of preparing chromatography-size agarose beads by including within an
30 agarose gel a macromolecular hydrocolloid such as sodium alginate, potassium lambda carrageenan, carrageenan, hydroxymethylcellulose, sodium carboxymethylcellulose, and the like. Upon drying the agarose beads the macromolecular hydrocolloid becomes coagulated within the
35 pore of the agarose. Upon rehydration, the macromolecular hydrocolloid dissolves, leaving the porosity

- 4 -

of the gel substantially intact for its intended use in chromatography.

U.S. 4,952,686 to Renn et al., discloses an alloy gum of cassia gum and a gelling and thickening agent such as carrageenan, agar, agarose, hydroxyethyl-cellulose, carboxymethylcellulose, dextran, and the like. This alloy gum when dried and ground into a powder can be readily dissolved in water to form a clear, stable colloidal solution.

Japanese patent publication 04/08,257 (92/08,257) (CA 116: 172746C) discloses the manufacture of dry konjac, which can be soaked in water to restore its original state and organoleptic properties, by mixing konjac with mono- and/or oligosaccharides such as glucose, sucrose, maltose, lactose and fructose, and then drying the mixture.

WO 91/19424 (PCT published application) discloses hydrated microparticulate beads as a fat substitute composed of a hydrous hydrocolloid gel, a metal capable of causing gellation, and an ionic polysaccharide such as alginate, pectate, and sodium carboxymethylcellulose.

Despite the extensive art as exemplified above relating to hydrocolloids and microparticulate forms thereof, no universally applicable techniques for drying and rehydrating such microparticulates without resulting in agglomeration of the microparticles and failure to disperse in water have been disclosed in the art. This is perhaps not surprising since gel-forming hydrocolloid microparticles exhibit very strong propensities to aggregate when wet or even in the presence of limited moisture such as when the dry microparticles are stored in contact with air. In fact, microparticulates made from gel-forming hydrocolloids alone cannot be dried and then rehydrated without specialized drying techniques to prevent agglomeration, since the dried agglomerates will not disperse or will disperse very poorly in the

- 5 -

presence of water upon attempted rehydration.

Agglomerated microparticulates cannot be used as a fat substitute since they do not possess the required organoleptic properties. It is therefore essential that
5 dried microparticulates be capable of rehydration to their original size and shape in order to closely mimic the organoleptic properties of fat, especially in oil-in-water emulsions. This problem of agglomeration when rehydrated is not shared, or is shared to only a limited
10 extent, with larger size hydrocolloid particles such as those disclosed in U.S. 3,527,712 and U.S. 4,952,686.

Hydrocolloid microparticulates that can be dried without necessitating special drying techniques and
15 processes for their production are provided by the present invention. The processes described herein provide substantially dry, rehydratable, water-dispersible, gel-forming, porous hydrocolloid microparticulates comprising:

- 20 A) a gel-forming hydrocolloid which comprises the matrix of the porous microparticulates; and
 B) at least one water-soluble, non-gelling, hydration-enhancing hydrocolloid;
- wherein the component A) matrix contains component B)
25 internally within its porous structure, and wherein component B) can also be present as a full or partial coating on the outer surfaces of the microparticulates. The dried microparticulates, even when prepared in the form of a coagulate, can be successfully
30 rehydrated to any desired extent, including aqueous dispersions thereof, without aggregation problems. Also, if desired, and in order to facilitate redispersion, dry coagulate forms of the microparticulates can be ground or otherwise comminuted
35 without harm to the microparticulates.

In a first embodiment of the process of the

- 6 -

invention, the process is carried out in the following steps:

- 5 A) preparing microparticulates of a gel-forming hydrocolloid by any operable technique, including those already known to the art;
- B) contacting the hydrocolloid microparticulates with at least one water-soluble, non-gelling, hydration enhancing hydrocolloid in an aqueous medium; and
- 10 C) drying the resulting hydrocolloid microparticulates.

 The hydrocolloid microparticulates produced by the above process are substantially dry, water-dispersible, porous, gel-forming hydrocolloid microparticulates
15 having occluded in the pores and on at least a portion of the outer surfaces thereof the water-soluble hydration enhancing hydrocolloid material.

 In a second embodiment of the process of the invention, the process is carried out in the following
20 steps:

- A) forming an aqueous composition comprising at least one gellable hydrocolloid and at least one water-soluble, non-gelling, hydration enhancing hydrocolloid;
- 25 B) forming hydrocolloid microparticulates from the aqueous composition of step A); and
- C) drying the resulting hydrocolloid microparticulates.

 The hydrocolloid microparticulates produced by the
30 above process are substantially dry, water-dispersible, gel-forming hydrocolloid microparticulates containing at least internally in the pores thereof a water-soluble, non-gelling, hydration enhancing hydrocolloid.

35 Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities

- 7 -

of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The gel-forming hydrocolloids used in the present invention for the manufacture of the matrix of the substantially dry microparticulates of the invention include but are not limited to the following: agars; agaroses; algins; low methoxyl pectins; gellans; K-carrageenan; ι -carrageenan; furcellaran; β -carrageenan; curdlan; chitosan; konjac glucomannan and derivatives thereof including heat stable cold-melt konjac glucomannan; cellulose derivatives; starches; and mixtures of two or more of the foregoing, as well as hydrocolloid mixtures such as xanthan/locust bean gum; locust bean gum/agar; cassia/agar; cassia/xanthan; konjac/xanthan; carrageenan/locust bean gum; konjac/carrageenan; and konjac/starch. The gel-forming hydrocolloid mixtures given above are employed in a weight ratio of from 80:20 to 20:80, preferably 60:40 to 40:60. When used herein, the term "konjac" should always be understood as referring to the glucomannan derived from konjac and specifically from species of *Amorphophallus* including, but not limited to, *A. oncophyllus* and *A. rivieri*, unless indicated otherwise.

The above gel-forming hydrocolloids can be present in their native state, or can be partially depolymerized or in the form of their derivatives, provided they form gels in such variant forms. Hydrocolloids can be selected that are thermoreversible, such as agar, agarose, K-carrageenan, ι -carrageenan, β -carrageenan and xanthan/locust bean gum, or thermoirreversible, such as alkali-set konjac, curdlan, and calcium alginate.

It is to be understood that while some of the above hydrocolloids will form gels without further treatment, many others require conversion to their potassium and/or

- 8 -

alkaline earth metal salts, such as the calcium or magnesium salt, and such salt forms are the gel forming hydrocolloids used in the invention. Methods for preparing such salts are well known in the art and do not
5 comprise part of the present invention.

Heat stable, cold-melt konjac is particularly preferred for use herein as a gel-forming hydrocolloid, since heat-stable properties are ideal for use in food-stuffs that require heat processing. Carrageenans are
10 also preferred gel-forming hydrocolloids.

The water-soluble, non-gelling, hydration enhancing hydrocolloid materials that can be used alone or in combinations in the practice of the invention are water-soluble, non-gelling hydrocolloids such as the following:
15 ing: galactomannans, e.g., water-soluble locust bean gum, guar gum, cassia, tara, and the like; water-soluble forms of konjac; starches, such as corn, potato, cereal, and tapioca; water-soluble cellulose derivatives, e.g., carboxymethylcellulose and hydroxymethylcellulose and
20 their sodium salts; water-soluble synthetic polymers, e.g., linear polyacrylamide, PVA, PEG, PEO, PVP, and the like; λ -carrageenan or the sodium salts of algin or pectin; water-soluble xanthan gum; and the like.

The substantially dry, rehydratable, non-aggregating, water-dispersible, gel-forming hydrocolloid microparticulates of the invention have an average
25 diameter when rehydrated in the range of 0.1 to 150 microns, preferably 1 to 50 microns, and more preferably from 5 to 30 microns. They are preferably substantially
30 spheroidal in shape, although other physical forms of the microparticulates can be made, depending on the manufacturing process, including ovoids, teardrops, and irregular shapes. A substantially spherical form is the most desirable shape since this shape best mimics the
35 lubricity obtained by an oil-in-water emulsion. Upon

- 9 -

rehydration of the dried substantially spherical micro-particulates, they return to their original pre-dominantly spherical shape and size. This is most important in order to mimic the size and shape of oil droplets in oil-in-water emulsions. The more preferable size of from 5 to 30 microns is close to the optimum size most often present in the oil droplets in an oil-in-water emulsion. Also, the dried microparticulates can be readily rehydrated to soft, non-aggregated, non-gritty microparticulates that exhibit the desired creamy mouthfeel of an oil-in-water emulsion.

In the first embodiment of the process of the invention, step A) is carried out by forming microparticulates of the gel-forming hydrocolloid. Many methods are known for forming such microparticulates, such as by spraying aqueous hydrocolloid sols or mixtures into air, hot water, or an organic solvent, e.g., a C₁-C₄ alkanol, or by forming hydrocolloid aqueous emulsions with organic water-immiscible solvents. Also, it was discovered that microparticulates can be formed with cold melt konjac by aspirating aqueous hydrocolloid mixtures into hot water.

A particularly suitable spray process is carried out by heating a gel-forming hydrocolloid in water, at a concentration of hydrocolloid of from 1 to 20%, preferably 0.5 to 2.0% by weight, based on the weight of water. The resulting solution or sol is then treated, as needed, with a gelling cation such as potassium, calcium or magnesium. The resulting aqueous mixture is then converted to an aerosol form in air using a spray nozzle. The aqueous droplets solidify when the gel temperature for the particular hydrocolloid is reached.

Alternatively, the heated solution or suspension is emulsified in a hot oil with stirring at a temperature above the gelling temperature of the hydrocolloid, with the addition of a gelling cation as needed, either

- 10 -

before or after emulsification. The temperature of the emulsion is then lowered while stirring is continued to produce the gelled microparticles. The oil is preferably a food grade oil such as a vegetable oil, including corn oil, peanut oil, sunflower oil, and olive oil. The ratio of hydrocolloid solution or suspension to oil is advantageously from 10:90 to 80:20, preferably from 30:70 to 60:40 by volume. The resulting microparticles are separated from the oil by filtration or centrifugation, and washed, e.g., with ethyl acetate or excess water to remove residual oil. It should be noted that the above emulsion process does not necessarily involve cooling of the system. For example, heat stable konjac microparticulates can be made by emulsifying an alkaline or pH adjusted cold-melt konjac sol in oil, and then heating the emulsion to gel the emulsified droplets into microparticulates.

In addition, microparticulates can be formed from the heated solution or suspension by changing the pH until gelling occurs; by the addition of synergistic hydrocolloid gelling agents; by spraying into a bath containing a gelling cation; or by metering in a gelling cation at the spray nozzle for conversion into an aerosol form.

In step B) of the first process embodiment, the hydrocolloid microparticulates formed in step A) preferably present in a concentration of from 0.2 to 20%, more preferably 0.5 to 5% by weight, are contacted with a solution of the water-soluble, non-gelling, hydration enhancing hydrocolloid in water. The concentration of the water-soluble hydrocolloid in water is not critical. Generally, a concentration of 0.01 to 10% by weight, preferably 0.5 to 2% by weight is employed. The temperature of the solution is also not critical, and external heating is not required. However, temperatures from 20° to 30°C are conveniently employed.

- 11 -

Contact time can be from 1 to 24 hours. The micro-
particles are then separated from the aqueous solution
of water-soluble hydrocolloid by any suitable method
such as by filtration or centrifugation. The separated
5 microparticles are coated on the external surfaces
thereof with the aqueous solution of the water-soluble
hydrocolloid, or are carried in the aqueous solution
depending on the quantity of aqueous solution present.
In addition, since the microparticles contain pores
10 which are large enough to admit the above solution,
coating of the walls of the pores will occur, and
although this is not required to obtain the benefits of
this embodiment of the process for non-aggregation
properties, it is required in order to obtain rapid and
15 complete rehydration of the dried microparticles from
step C) below.

In step C) of this process embodiment, the coated
microparticles are dried. Specialized drying procedures
are not required, and drying can be effected by any
20 desired technique, such as by coagulating in a water-
miscible organic solvent such as an alcohol, and then
oven drying; forced hot air drying; spray drying;
fluidized bed drying; azeotropic washing; freeze drying;
vacuum drying; and the like, or any combination of the
25 above. Especially useful as a coagulating solvent is
isopropyl alcohol containing from 0 to 20% by volume of
water. Oven drying alone can also be employed, but is
not always uniformly satisfactory with some gel-forming
hydrocolloids such as konjac.

30 The resulting substantially dry hydrocolloid micro-
particulates contain a layer of the water-soluble hydro-
colloid occluded on the outside surfaces of the micro-
particles as well as an internal coating on the walls of
the pores therein. This process is the preferred
35 process for forming the dry microparticulates of the
invention, since the dry microparticulates resulting

- 12 -

from this embodiment of the process can be rehydrated to any desired extent and can be readily dispersed in water, regardless of the gel-forming hydrocolloid selected. Upon rehydration, the microparticulates
5 reassume essentially the same size and shape they possessed prior to drying.

In the second process embodiment of the invention, a heated aqueous composition is formed containing the gel-forming hydrocolloid and the water-soluble hydrocolloid.
10 The gel-forming hydrocolloid or mixture of hydrocolloids is present in a concentration of from 0.2 to 20%, preferably 0.5 to 5% by weight, and the water-soluble hydrocolloid is present in a concentration of from 0.01 to 10%, preferably 0.5 to 2% by weight. The above per-
15 centages by weight are based on the weight of water. Also present is the gelling cation, if needed, or the gelling cation can be added in step B). The heated aqueous composition is formed and maintained at a temperature above the gelling temperature of the gel-forming hydrocolloid.
20

Step B) of this second process embodiment is carried out as described above for step A) of the first process embodiment, i.e., hydrocolloid microparticulates are formed from the above heated aqueous composition, e.g.,
25 using a spray or emulsion procedure.

Step C), the drying step, is then carried out as disclosed above for step C) of the first process embodiment.

This second process embodiment produces dry,
30 rehydratable, porous, non-aggregating, water-dispersible gel-forming hydrocolloid microparticulates containing the water-soluble hydrocolloid as part of the microparticulate structure. While the resulting microparticles can be dispersed in water, and have a much
35 reduced tendency to aggregate when hydrated, their dispersion in water is not always as uniformly complete

- 13 -

as with microparticulates produced by the first process embodiment.

It is also of course possible to combine both processes, such as by adding water-soluble hydrocolloid, which can be the same or different from that used in step B), to the aqueous solution or suspension of gel-forming hydrocolloid in step A) of the first process embodiment. In this process variation, the water-soluble hydrocolloid is present both internally and externally in the resulting microparticulates. This combined process variant is especially useful where gel-forming hydrocolloids or mixtures thereof are employed that normally produce severe aggregation problems with hydrated microparticulates formed from them.

Heat stable, cold-melt konjac glucomannan is advantageously employed as the gel-forming hydrocolloid for forming the microparticulates of the invention. Methods for the preparation of heat stable, cold-melt konjac glucomannan are disclosed in PCT patent application publication No. WO 93/02571 (PCT/US92/06591) which is incorporated herein by reference. A convenient method is as follows. Konjac powder is dissolved in water, by heating the water until a solution of the konjac powder is obtained. Generally, a temperature of from 50-100°C, preferably 75-95°C can be employed. Then a water-soluble base or basic salt, preferably potassium carbonate, is added with mixing to the heated solution to a pH of 10 to 11.5 to form a konjac gel. The konjac gel is isolated from the remaining aqueous medium and cooled until the gel cold-melts into the form of a sol. Cooling is usually carried out at a temperature of from 0 to 10°C, preferably at 2 to 6°C. For use in a process of the invention for forming substantially dry, rehydratable, water-dispersible, porous, gel-forming hydrocolloid microparticulates, the sol from step C) above can be used as the gel-forming hydrocolloid in

- 14 -

step A) of each process embodiment.

The microparticulates formed by the processes of the invention can be rehydrated to any desired extent, that is, controlled hydration can be effected, enabling a
5 wide range of control over the consistency of the product. The dry microparticulates provide important commercial advantages in terms of storage and shipping space, shipping weight, and in the ability to accurately control the degree of rehydration. In addition, during
10 storage and shipping, the possibility of microbial contamination is much reduced compared to hydrated microparticulates.

The microparticulates of the invention are especially useful when rehydrated as a bulking agent and
15 for their organoleptic properties as a replacement for all or part of the fat components of comestibles. For this use, they may be part of a mixture that may also contain other ingredients such as texturizers like gelling carrageenans and/or konjac; mouthfeel imparting
20 agents such as xanthan, locust bean gum, and guar gum; vitamin and mineral supplements, flavoring agents; oils; pigments like TiO_2 ; and the like.

The microparticulates of the invention when rehydrated can be used in place of all or part of a
25 water-in-oil or oil-in-water emulsion in foodstuffs containing such emulsions, such as salad dressings, mayonnaise, sauces, gravies, desserts, milk products, puddings, fondues, dips, confections, ice cream, yogurt, mousse, frostings and icings and the like.

Another important use for the dry microparticulates of the invention is the encapsulation of various
30 materials which are added to the aqueous hydrocolloid compositions prior to microparticulate formation. Such materials include natural flavoring agents; food
35 additives such as synthetic flavoring agents, anti-oxidants and acidulants; food processing aids; medicinal

- 15 -

and biological materials such as enzymes, fungicides, antibiotics, antibacterial agents, biocides, nutrients such as vitamins and minerals, hormones, cells, and the like; colorants; odorants; chromatography media; agglutination media for diagnostics; nephelometric enhancers; immobilization matrices; herbicides; insecticides; pesticides; animal feed supplements; fertilizers; surfactants; detergents; and immunoassay reagents. Also useful for encapsulation are pharmaceutical actives including, but not limited to: analgesics such as acetaminophen (APAP); antihistamines such as chlorpheniramine maleate; decongestants such as pseudoephedrine HCl; cough suppressants such as dextromethorphan HBr; antibiotics such as tetracyclines and erythromycins; anticonvulsants such as diphenylhydantoin; and thyroid stimulants such as laevothyroxine.

EXAMPLES

Example 1

Preparation of 1.0% w/w cold-melt konjac sol

Cold tap water (100 g) was weighed into a 250-ml beaker and the tare weight of water and beaker recorded. Using an overhead mixer, 1.0 g of konjac powder was suspended in the cold water. The konjac was added slowly to prevent clumping. With continuous agitation, this suspension was heated in a hot water bath at $\geq 85^{\circ}\text{C}$ approximately 60 minutes during which time the konjac powder became a sol. The beaker was placed on a balance and sufficient water added to replace that lost by evaporation. The added water was mixed thoroughly. To the konjac sol was added 0.75 ml of 1.0 M potassium carbonate (0.75 ml/gram of konjac) and mixed in thoroughly using an overhead mixer. The konjac/potassium carbonate sol was heated in a hot waterbath

- 16 -

until the temperature at the center reached 85°C and was held at that temperature or slightly above for 20 minutes. The gelled konjac was removed from the water-bath, cooled to room temperature, and placed in an ice-bath to cold-melt the konjac gel to a sol (ca. 4°C).
5 The time required to obtain the cold-melt sol was approximately 2 hours. Longer periods are required for higher konjac concentrations and slicing the gel into small pieces helps reduce the amount of time needed to
10 obtain a cold-melt sol. The thin skin on the surface of the cold-melt sol, which frequently formed, was removed.

The pH of the konjac cold-melt sol can be adjusted to any level without affecting subsequent gelation.

15 Example 2

Formation of konjac heat stable cold-melt micro-particulates

To 100 g of the konjac sol prepared in Example 1,
20 was added 0.10 g of carboxymethylcellulose (CMC) dissolved in 10 ml of cold water. While maintaining the sol mixture at ice-bath temperature (0-4°C), the sol mixture was neutralized by adding a sufficient quantity of 0.1 N HCl to adjust the pH to 7.0, while stirring and
25 monitoring with a pH meter probe. A Silverson® L4R mixer was set up with the emulsion screen on the standard two-arm mixing unit. Using a ringstand and clamp, a 1500-ml beaker containing 1 liter of preheated (ca. 90°C) Wesson® oil was placed in a boiling water
30 bath located on the Silverson® mixer platform under the emulsifier. The mixing arm was lowered into the hot oil and the mixer started at the maximum setting. The neutralized, CMC-containing, cold-melt konjac sol was slowly added, by pouring, to the heated oil. After the
35 addition of the sol to the hot oil was completed, mixing

- 17 -

was continued for one minute. The aqueous, microparticulate-containing layer was distributed into 150-ml centrifuge bottles (ca. 125 ml in each), about 25 ml of 30% isopropyl alcohol containing 0.01% CMC was
5 added to each, the bottles were balanced, and then centrifugation was effected at 6000 rpm for 10 minutes, during which time a pellet formed which contained the microparticulates. The oil layers were removed by decantation, combined, and held for reuse. The aqueous
10 alcohol layer was then removed, also by decantation. The pelleted microparticulates were combined using about 3X volume of 0.1% CMC (aq.) solution, followed by redispersion using a Silverson® mixer, again using the maximum speed setting. This dispersion, containing the
15 microparticulates, was transferred to 50-ml centrifuge tubes and centrifuged at 1000 rpm for 5 minutes to remove debris and large beads and aggregates. The pellets were discarded and the supernatants, containing the microparticulates, were combined and boiled for one
20 hour using a stirring hot plate. The Silverson® mixer was again used to ensure complete suspension and another 5 minute, 1000 rpm cycle used to remove gel debris. (If desired, the microparticulates can be pelletized by centrifugation at 4000 rpm for 10-15 minutes).
25 Microparticulates obtained by this procedure contained 94% water and 0.48% oil (by ether extraction method). Room temperature storage stability of the microparticulates was achieved by two methods. The first of these was by transferring the microparticulates
30 to 30% (v/v) isopropyl alcohol (aq) and the other was by suspending them in 1% aqueous CMC and coagulating this suspension in isopropyl alcohol, recovering the coag, then drying.

35

- 18 -

Variations of this procedure gave the following results:

	<u>VARIABLE</u>	<u>RESULT</u>
	Mixing time	
5	1 minute	small microparticulates (1-20 microns)
	5 minutes	larger microparticulates (20-200 microns)
10	Temperature of oil	
	50°C	mixture of sizes
	65°C	good, small micro- particulates
15	85°C	good, small micro- particulates
	90°C	Very good, small micro- particulates
	Mixer/chamber	
20	Waring® blender	variable ratios of micro- particulates and debris, depending on the chamber used
25	Silverson® mixer	good to very good microparticulates depending on the temperature and speed
30	Ratio of cold-melt sol to oil	
	1:10	very good small micro- particulates
	1:1	good microparticulates, some debris
35		

- 19 -

Surfactant added to oil

Tween® 80 no discernible effect
(polyoxyethylene (20)-
sorbitan mono-oleate)

5

Other oil used

Castor oil good microparticulates
 but more difficult to
 recover

10

Konjac preparation used

Crude good microparticulates,
 considerable debris
Alcohol washed good microparticulates,
 less debris
Clarified goods microparticulates,
 little debris

15

Example 3

20 Formation of microparticulates by aspirating konjac
cold-melt sol containing carboxymethylcellulose into hot
water.

25 One liter of a 1.5% konjac cold-melt sol using
clarified konjac was prepared by adding 15 g of clari-
fied konjac to one liter of water and heating to 85°C to
effect dissolution. This sol was gelled by adding 7.5
ml of 1 M K₂CO₃, followed by subsequent heating in a
boiling water bath. This gel was then placed in an ice
30 bath to produce the cold-melt konjac sol. To this was
added 0.1 g of carboxymethyl cellulose (CMC) dissolved
in 15 ml of water and the sol was then neutralized using
0.1 N HCl. Portions of this were drawn through an
aspirator into a stream of hot water. Small micro-
35 particulates were formed, along with fine debris. The
microparticulates were collected by centrifugation.

- 20 -

The microparticulates were dried overnight in a forced air oven. When the dried microparticulates were rehydrated by the addition of water, the rehydrated microparticulates separated into individual entities and did not agglomerate.

Example 4

Preparation of cold-melt konjac microparticulates followed by treatment with carboxymethylcellulose solution

Clarified konjac was used to prepare a 200 ml of 0.5% cold-melt konjac sol using the method described in Example 1. To this was added about 20 ml of a cold aqueous solution containing 0.02 g CMC. The sol was adjusted to pH 7 using 0.1 N HCl. This sol was transferred to a chilled paint sprayer (Wagner Heavy Duty Power Painter®, Wagner Spray Tech Corporation) bottle fitted with a trigger controlled nozzle. The cold-melt konjac sol was sprayed into a receiving tray containing 83% isopropyl alcohol (aq) at a depth of about one inch. The height of the sprayer nozzle (0.8mm i.d.) to the surface of the alcohol was adjusted to about 18 inches and spraying was done so that heavy streaming was avoided. Excellent konjac microparticulates (25-100 micron diameter) were obtained. Smaller microparticulates were prepared using a 0.6mm inside diameter sprayer tip, and in each case the microparticulates were recovered by centrifugation. The microparticulates were suspended in a 1% CMC aqueous solution and the mixture stirred at room temperature overnight. Two methods were used for drying, the first consisting of spreading the mixture in an appropriate vessel and drying overnight in a forced-air oven. The second method used was coagulation of the suspension in isopropyl alcohol, recovering the coagulate, then drying it in a forced-air

- 21 -

oven at 55°C. When water was added to the dried ground microparticulates and the mixture dispersed using a Silverson® L4A homogenizer, the rehydrated microparticulates separated into individual entities and did not aggregate.

Example 5

Preparation of carrageenan microparticulates co-dried with carboxymethylcellulose

10

A 2.0% by weight of K-carrageenan in distilled water at about 85°C was sprayed into the air to form microparticulates, using the spray equipment of Example 4. The resulting carrageenan microparticulates were divided into four equal portions and each portion was treated and dried or just dried by one of the following procedures:

- A) coagulation in 1 volume of 99% isopropyl alcohol, followed by oven drying;
- 20 B) mixing the microparticulates with an equal volume of 1% carboxymethylcellulose, then coagulation of the mixed microparticulates with 1 volume of 99% isopropyl alcohol, followed by oven drying;
- 25 C) oven drying the water slurry of microparticulates directly;
- D) mixing the microparticulates with an equal volume of 1% carboxymethylcellulose, followed by oven drying.

30 The dried microparticulates were evaluated by dispersing coarsely-ground particles with low-shear mixing in a quantity of water equal to the original hydrated microparticulate weight, then the microparticulates were allowed to rehydrate for 1 hour, followed by high shear mixing in a Silverson® mixer.

35

- 22 -

Visual observation of the resulting sols was made, and the microparticulates were examined under a microscope for degree of rehydration and dispersion/aggregation.

The results are set forth in Table 1 below:

5

Table 1

	Treatment and Drying Procedure	Sol	Microparticulates	
			Rehydration	Dispersion
10	A	soft paste	incomplete, many small micro- particulates	good, no aggregation
15	B	viscous sol	complete, rounded micro- particulates	good, no aggregation
20	C	100% settling	poor, mostly shrunken micro- particulates	poor, aggregation
25	D	50% settling	partial, many shrunken micro- particulates	good, no aggregation

While the oven dried microparticulates of Treatment D did not rehydrate completely in a 1 hour treatment period with water, longer hydration times resulted in substantially complete hydration.

30

Example 6

Preparation of heat stable konjac microparticulates with and without carboxymethyl cellulose.

35

A) A 2.0% by weight hot solution of konjac sol was sprayed using the spray equipment of Example 4. Before the hot solution of konjac sol reached the spray nozzle, a 10% by weight aqueous solution of K_2CO_3 was metered in at a rate that provided 0.2 g of K_2CO_3 per gram of konjac. The resulting konjac microparticulates were partially dehydrated in 2 volumes of 85% isopropyl alcohol, the partially dehydrated microparticulates

40

- 23 -

collected by vacuum filtration, and dried in a forced air oven for 2 hours at 140°F [60°C].

B) Partially dehydrated konjac microparticulates were prepared according to the procedure given in A) above, except that the 2.0% hot solution of cold-melt konjac sol also contained 0.7% by weight of carboxymethyl cellulose.

C) One gram of the microparticulates prepared according to procedure A) above was dispersed in 100 g of distilled water using low shear mixing. One gram of the microparticulates prepared according to procedure B) above was also dispersed in 100 g of distilled water using the low shear mixing. Both dispersions were gently stirred for 10 minutes and allowed to stand without stirring for periods of 10 minutes, 1 hour, 2 hours, and 24 hours. After standing for each of the above periods, a sample was removed and centrifuged at 2000 rpm in a graduated centrifuge tube. The comparative degree of rehydration was determined by measuring the volume of the microparticulates after centrifugation.

The results are set forth in Table 2 below.

Table 2

holding time	sample A (no CMC)	sample B (with CMC)
	rehydration volume	rehydration volume
10 minutes	6 ml	20 ml
1 hour	8 ml	25 ml
2 hours	8 ml	25 ml
24 hours	8 ml	25 ml
2 hours*	8 ml	50 ml

*This sample was subjected to high shear in a Silverson® homogenizer for 3 minutes.

- 24 -

As can be seen from the results obtained in Table 2, the partially dehydrated microparticulates from procedure A did not rehydrate even after a 24 hour period. These microparticulates had a dry, gritty texture and could not be used as a fat substitute in a low fat comestible. The partially dehydrated microparticulate samples from procedure B on the other hand rehydrated well and had a smooth, creamy, fat-like feel. These rehydrated microparticulates are highly effective and useful as a fat substitute in low fat comestibles.

Example 7

Preparation of konjac microparticulates with starch

Konjac/starch microparticulates were made by the following process:

Forty grams of konjac flour was dispersed in 600 grams of 60°C water in a food processor for 15 minutes to form a smooth paste. Forty grams of pre-gelatinized starch (National 1215) and 40 grams of potato starch (Avebe Perfectamyl® D-12) were added to the paste, followed by 130 grams of water. This was mixed for 15 additional minutes. The material was then cooled to 25°C and placed in a Hobart® mixer. Twelve grams of trisodium phosphate pre-dissolved in 100 grams of water was added. The konjac-starch paste was poured into crystallizing dishes, and left overnight in a refrigerator at 10°C. The gels were particulated using a Silverson® mixer at high speed.

The resulting microparticulates were divided into three equal portions, and each portion dried by one of the procedures (I-III) set forth below.

- I) drying in one volume of 98% isopropyl alcohol.
- II) mixing with an equal volume of a 1% solution of

- 25 -

carboxymethylcellulose and then coagulating in one volume of 98% isopropyl alcohol.

III) air drying the microparticulates directly in a 50°C forced air oven.

5 The dried microparticulates were evaluated by dispersing 1 gram of the microparticulates in 100 grams of water. The microparticulates were allowed to rehydrate for one hour, subjected to shear in a Silverson® mixer, and observed. The results obtained
10 are set forth in Table 3 as follows:

Table 3

15	Treatment and drying conditions	Dispersibility
	I (98% IPA)	good
20	II (1% CMC + IPA)	good
	III (oven drying)	poor

Example 8

25 Preparation of oil-encapsulated konjac micro-particulates

Clarified konjac was used to prepare 250 ml of 0.5% cold-melt konjac sol using the method described in
30 Example 1. Using a Silverson® L4A homogenizer at maximum speed with the emulsion screen in place, 250 ml of Wesson® oil at room temperature was added to the 250 ml of cold-melt konjac sol. Upon completion of the addition, emulsification was continued for one minute.

35 To the resulting oil-encapsulated konjac microparticulates there was added 300 ml of a 0.01% solution of carboxymethyl cellulose in aqueous isopropyl alcohol (30%). This mixture was stirred for one hour.

- 26 -

An equal amount of 85% isopropyl alcohol was added and the mixture allowed to stand overnight. The microparticulates were recovered by centrifugation and dried at 55°C in a forced air oven. When water was added while mixing, the microparticulates rehydrated well and were non-aggregated.

Example 9

Ranch style dressing formulations.

10

Four ranch style dressing formulations (Formulations A through D) are made by the following procedure:

A dry blend is made containing sugar, buttermilk powder, xanthan gum, potassium sorbate, calcium disodium EDTA, and egg yolk powder. This dry blend is dispersed into water using high shear, and mixed for 10 minutes. Vinegar, salt, mustard powder, and buttermilk flavor are then added to the dispersion, followed by the addition of rehydrated konjac microparticulates prepared by the process of Example 2 and/or vegetable oil. Then garlic powder, onion powder, ground black pepper, and parsley are added, and the resulting dressing formulation mixed for 5 minutes.

The composition of each formulation is given in Table 4 below.

30

35

- 27 -

Table 4

	FORMULATION A		FORMULATION B		FORMULATION C		FORMULATION D	
	FULL FAT		NO FAT		10% FAT, 35% BEAD		10% FAT, 25% BEAD	
	%	weight	%	weight	%	weight	%	weight
<u>Ingredient</u>								
Water	48.35	241.75	49.44	247.2	38.89	194.45	49.44	247.2
Vinegar-120-gr.	5	25	5	25	5	25	5	25
Sugar	4	20	4	20	4	20	4	20
Buttermilk Powder	3.5	17.5	3.5	17.5	3.5	17.5	3.5	17.5
Egg Yolk Powder	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5
Salt	2	10	2	10	2	10	2	10
Xanthan Gum	0.4	2	0.4	2	0.4	2	0.4	2
Garlic Powder	0.27	1.35	0.09	0.45	0.09	0.45	0.09	0.45
Onion Powder	0.27	1.35	0.09	0.45	0.09	0.45	0.09	0.45
Gr. Blk Pepper	0.23	1.15	0.06	0.3	0.06	0.3	0.06	0.3
Ca Disodium EDTA	0.01	0.05	0.01	0.05	0.01	0.05	0.01	0.05
Parsley	0.02	0.1	0.01	0.05	0.01	0.05	0.01	0.03
Mustard Powder	0.05	0.25	0.05	0.25	0.05	0.25	0.05	0.25
Konjac Microparticulates	0	0	34.45	172.25	35	175	24.45	122.25
Buttermilk Flavor	0.3	1.5	0.3	1.5	0.3	1.5	0.3	1.5
vegetable oil	35	175	0	0	10	50	10	50
potassium sorbate	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
TOTAL	100	500	100	500	100	500	100	500

Formulation A is made as a full fat control formulation. Formulation B is a no fat formulation. This formulation, in which rehydrated cold-melt konjac microparticulates are used in place of all of the vegetable oil, possesses good organoleptic properties. Formulation C which contained 10% vegetable oil and 35% rehydrated konjac microparticulates, and Formulation D which contains 10% vegetable oil and 25% rehydrated konjac microparticulates, are similar in both texture and flavor to full fat Formulation A, and exhibit excellent organoleptic properties.

- 28 -

Example 10

Ranch style dressing formulations.

Three ranch style formulations (Formulations E through G) are made by the procedure of Example 9 except that rehydrated carrageenan microparticulates prepared in accordance with the procedure of Example 5 (drying procedure B) are substituted for rehydrated konjac microparticulates in Formulations B through D respectively.

Formulation E possesses good organoleptic properties, and Formulations F and G possess excellent organoleptic properties, and are similar in both texture and flavor to full fat Formulation A.

Example 11

Mayonnaise type dressing (3-25% fat).

A spoonable mayonnaise type dressing is prepared containing the following ingredients:

<u>Ingredients</u>	<u>% by wt.</u>
Water	QS
rehydrated carrageenan microparticulates	5.0-50.0
25 vegetable oil (soybean)	3.0-25.0
sugar	6
Avicel® CL-611 (microcrystalline cellulose)	3.5
Vinegar (120 gr.)	3.5
30 Salt	2.5
Gelex® Instant Starch-Amaizo™	1.0-4.0
Egg Yolk Solids - Hanningson's type Y-1	1.5
lemon juice	1
Xanthan Gum-Keltrol®	0.4
35 Viscarin® SD 369 (carrageenan powder)	0-0.3
Mustard Powder	0.25
potassium sorbate	0.1

- 29 -

Quest® Mayonnaise Flavor 7R 13774	0.1
Ca disodium EDTA	0.01
Carotenal Solution (1.4% Beta Carotene)	<u>0.0015</u>
TOTAL	100.00

5 The above dressing is prepared as follows:

 The microcrystalline cellulose is mixed with the water for 5 minutes in a Silverson® mixer. The carrageenan powder, if present, is dry blended with part
10 of the sugar and added to the above water mixture and mixed for 5 minutes in the bowl of a Hobart® mixer. A dry blend of xanthan gum, egg yolk solids, starch, the remainder of the sugar, and potassium sorbate is prepared and added slowly with mixing to the bowl of the
15 Hobart mixer, with mixing continuing for 10 minutes. Rehydrated carrageenan microparticulates, prepared by the process of Example 5 (drying procedure B) are slowly added to the bowl. The vegetable oil, beta carotene, and mayonnaise flavor are blended, added to the bowl and
20 mixed for 5 minutes. Then the lemon juice, vinegar, and calcium disodium EDTA are slowly added to the bowl with mixing. A blend of salt and mustard powder are added and mixed until smooth (about 10 minutes). The resulting mixture is then milled in a Fryma® mill at 0.3
25 mm, followed by de-aeration.

 The mayonnaise type dressing so produced is spoonable, homogeneous, and possesses organoleptic properties similar to those of a full fat mayonnaise.

30 Example 12

 Spread formulation (margarine type) containing 20 to 35% fat.

35 A spread formulation containing from 20 to 35% by weight of fat is formulated to contain the following ingredients:

- 30 -

<u>Aqueous Phase</u>		<u>% by wt.</u>
<u>Ingredients</u>		
5	Avicel® RC-591F (microcrystalline cellulose)	0.7 to 2.0
	Rehydrated microparticulates*	5.0 to 25.0
	xanthan**	0.07 to 0.2
	NaCl	1.80
10	K Sorbate	0.20
	Maltrin® 040	5.00
	flavor	0.05
	water	QS
15	* the rehydrated microparticulates are either rehydrated konjac microparticulates prepared by the process of Example 2 or carrageenan microparticulates prepared by the process of Example 5 (drying procedure B). They are used as a 1:1 replacement for oil/fat based on a 40% fat 20 content.	
25	** Iota carrageenan powder can also be included in addition to xanthan gum in a range of from 0.05 to 0.30% to enhance mouthfeel.	
<u>Lipid Phase</u>		<u>% by wt.</u>
<u>Ingredient</u>		
	soy oil	11.5
30	Ingot Soya	7.15
	palm oil	5.65
	Dimodan® OK ¹	0.35
	Triodan® R-90 ¹	0.25
35	¹ Emulsifiers	

- 31 -

The above lipid phase is based on a spread formulation containing 25% fat content. The above formulation can be varied to provide a spread formulation containing a lipid phase of from 20 to 35% and an aqueous phase of from 65 to 80%.

The above spread formulation is prepared as follows:

Aqueous Phase

The microcrystalline cellulose is dispersed in the water in a Silverson® mixer. Xanthan gum is then added with mixing. The remaining aqueous phase ingredients, except for the rehydrated microparticulates, are mixed into the above dispersion. The rehydrated microparticulates are added using minimum agitation to preserve their structural integrity. The resulting aqueous mixture is heated to to 50°C just prior to forming an emulsion with the lipid phase.

Lipid Phase

The ingot soya is melted in a hot water bath. The emulsifiers are then added to the liquid ingot soya at a temperature of 80-85°C. The soy and palm oil are heated together in a steam kettle to 65°C. The ingot soya-emulsifier mixture is cooled to 65°C and added to the soy and palm oil. The resulting mixture is then held for 15 minutes to temper the fat, and the mixture cooled to 50°C.

Emulsion formation

Using agitation in a Lightnin® mixer containing the lipid phase, the aqueous phase is added slowly to avoid the incorporation of air into the mixture. When the two phases are completely combined in the form of a water-in-oil emulsion, the mixture is passed through a margarine crystallizer to form the finished spread.

- 32 -

The finished spread has organoleptic properties similar to those of a full fat (40%) margarine spread.

Example 13

- 5 Preparation of a reduced fat shortening containing rehydrated cold-melt konjac microparticulates.

The quantities of Crisco® shortening given below are weighed and placed into Hobart® mixing bowls along with
 10 0.2-1.0 wt % (based on total weight of shortening and microparticulates) of a low HLB surfactant such as sorbitan monostearate, distilled monoglycerides, or polyglycerol esters. Rehydrated cold-melt konjac microparticulates prepared according to procedures B and
 15 C of Example 6 (2 hour rehydration period) are added in the quantities given below, except for the control. Homogeneous mixtures are formed by mixing the above components in the Hobart® mixing bowls for about 5 minutes.

20

<u>Component</u>		<u>Grams</u>			
	rehydrated konjac microparticulates	0	5	15	30
25	low HLB surfactant	0.5	0.5	0.5	0.5
	Crisco® shortening	99.5	94.5	84.5	69.5

Each of the above three compositions containing
 30 rehydrated konjac microparticulates are substantially similar to and essentially indistinguishable from the composition containing only the Crisco® shortening.

Example 14

- 35 Preparation of a reduced fat shortening containing rehydrated carrageenan microparticulates.

- 33 -

The process of Example 13 is repeated except that rehydrated carrageenan microparticulates prepared according to Example 5 (drying procedure B) are used.

Each of the resulting three compositions containing
5 rehydrated carrageenan microparticulates are substantially similar to and essentially indistinguishable in mouthfeel from the composition containing only the Crisco® shortening.

10

15

20

25

30

35

- 34 -

CLAIMS:

1. Substantially dry, rehydratable, water-dispersible, gel-forming, porous hydrocolloid microparticulates characterized by:

- 5 A) a gel-forming hydrocolloid which comprises the matrix of the porous microparticulates; and
 B) at least one water-soluble, non-gelling, hydration-enhancing hydrocolloid;

wherein the component A) matrix contains component B) internally within its porous structure, and wherein component B) can also be present as a full or partial coating on the outer surfaces of the microparticulates.

2. The microparticulates of claim 1 characterized in that the microparticulates when rehydrated have an average particle size diameter in the range of from 0.1 to 150 microns.

3. The microparticulates of claim 2 characterized in that the average particle size is from 1 to 50 microns.

4. The microparticulates of claim 2 characterized in that the average particle size is from 10 to 30 microns.

5. The microparticulates of claim 1 characterized in that the microparticulates are substantially spheroidal in shape.

6. The microparticulates of claim 1 characterized in that the gel-forming hydrocolloid is at least one of agar, agarose, algin, low methoxyl pectin, gellan, K-carrageenan, λ -carrageenan, furcellaran, β -carrageenan, curdlan, konjac glucomannan and derivatives thereof, chitosan, cellulose derivatives, starch, and gel-forming mixtures of the following: xanthan/locust bean gum, locust bean gum/agar, cassia/agar, cassia/xanthan, carrageenan/locust bean gum, konjac/xanthan, konjac/carrageenan, and konjac/starch.

- 35 -

7. The microparticulates of claim 1 characterized in that the water-soluble, non-gelling, hydration enhancing hydrocolloid is at least one water-soluble form of a galactomannan, a glucomannan, a starch, a cellulose derivative, λ -carrageenan, algin, pectin, xanthan, and a synthetic polymer.

8. The microparticulates of claim 7 characterized in that said water-soluble hydrocolloid is sodium carboxymethylcellulose.

9. The microparticulates of claim 1 characterized in that the gel-forming hydrocolloid is heat stable cold-melt konjac.

10. The microparticulates of claim 1 further characterized by having encapsulated therein at least one of a food additive, natural flavoring agent, antioxidant, acidulant, colorant, odorant, enzyme, fungicide, antibiotic, antibacterial agent, biocide, nutrient, hormone, cell, chromatography medium, agglutination medium for diagnostics, nephelometric enhancer, pharmaceutical active, immobilization matrix, herbicide, insecticide, pesticide, animal feed supplement, fertilizer, surfactant, detergent, or immunoassay reagent.

11. The microparticulates of claim 1 characterized in that the microparticulates also contain a food additive encapsulated therein.

12. A process for the preparation of the substantially dry, rehydratable, water-dispersible, gel-forming, porous microparticulates of claim 1 characterized by the steps of

A) forming hydrocolloid gel microparticulates from the gel-forming hydrocolloid,

B) contacting the hydrocolloid microparticulates with at least one water-soluble, non-gelling, hydration enhancing hydrocolloid in an aqueous medium, and

- 36 -

C) drying the resulting hydrocolloid micro-particulates.

13. The process of claim 12 characterized in that the microparticulates in step A) have an average
5 particle size diameter of from 0.1 to 150 microns.

14. The process of claim 13 characterized in that the microparticulates are substantially spheroidal in shape.

15. The process of claim 12 characterized in that
10 in step A) the gel-forming hydrocolloid is heat stable cold-melt konjac.

16. The process of claim 12 characterized in that step C) is carried out by either air drying, spray drying, oven drying, fluidized bed drying, freeze
15 drying, vacuum drying, or coagulating with a water-miscible organic solvent followed by oven drying.

17. The process of claim 16 characterized in that drying is carried out using isopropyl alcohol containing from 0 to about 20% by volume of water, followed by oven
20 drying.

18. A process for the preparation of the substantially dry, rehydratable, water-dispersible, gel-forming, porous microparticulates of claim 1 characterized by the steps of

25 A) forming an aqueous composition comprising at least one gellable hydrocolloid and at least one water-soluble, non-gelling, hydration enhancing hydrocolloid,

B) forming hydrocolloid microparticulates from the aqueous composition of step A), and

30 C) drying the resulting hydrocolloid microparticulates.

19. The process of claim 18 characterized in that the microparticulates in step B) have an average particle size diameter of from 0.1 to 150 microns.

35 20. The process of claim 19 characterized in that

- 37 -

the microparticulates are substantially spheroidal in shape.

21. The process of claim 18 characterized in that in step A) the gellable hydrocolloid is heat stable
5 cold-melt konjac.

22. The process of claim 18 characterized in that step C) is carried out by either air drying, spray drying, oven drying, fluidized bed drying, freeze
10 drying, vacuum drying, or coagulating with a water-miscible organic solvent followed by oven drying.

23. The process of claim 22 characterized in that drying is carried out using isopropyl alcohol containing from 0 to 20% by volume of water followed by oven
drying.

15 24. A fat substitute characterized by the rehydrated microparticulates of claim 1.

25. A comestible in which a water-in-oil or oil-in-water emulsion is present, characterized in that the rehydrated microparticulates of claim 1 are used
20 partially or completely in place of the oil to reduce the fat content of the comestible.

26. A low fat or no fat comestible containing the rehydrated microparticulates of claim 1.

25 27. A method of preparing a no fat or low fat foodstuff having good organoleptic properties characterized by the steps of

I) rehydrating the dry microparticulates of claim 1, and

30 II) adding the hydrated microparticulates to the foodstuff in place of part or all of the fat content thereof.

35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08860**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :B32B 9/00

US CL :428/403; 536/114, 126

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/403; 536/114, 126

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,153,020 (SINGER et al) 06 October 1992	1-23

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

06 OCTOBER 1994

Date of mailing of the international search report

08 NOV 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

E.ROLLINS BUFFALOW

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

Int. application No.
PCT/US94/08860

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-23

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08860

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-23, drawn to an article and process of making article, classified in Class 428, subclass 403 and Class 427, subclass 213.3.

Group II, claim(s) 24-26, drawn to a fat substitute, classified in Class 426, subclass 601.

Group III, claim(s) 27, drawn to a method of rehydrating, classified in Class 426, subclass 506.

The inventions listed as Groups I-II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The combinations are independent because they are not disclosed as being capable of use together. The process of Group I is not applicable in the method of Group III and rehydrating of Group III is not required in the method of Group I.